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The Properties of Graft Polymerized Polyvinyl Alcohol Fibers*

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Some vinyl compound such as styrene and methylmethacrylate were graft polymerized onto polyvinyl alcohol fibers mainly with the radiation of Co^{60} γ -ray, and some properties of those graft polymerized fibers were examined.

It was found that some favorable properties such as thermoplasticity and elasticity and water-resistivity could be imparted to polyvinyl alcohol fibers by this graft polymerization without much lowering the tensile strength and softening temperature.

INTRODUCTION

Recently a large number of studies on a different type of graft copolymer had been reported. The synthetic fibers made of these graft copolymers may be expected to have all properties of those components.

Under such consideration some of the authors¹⁾ had studied the preparation of a synthetic fiber made of the graft copolymer of acrylonitrile (AN) onto polyvinyl alcohol (PVA). A proper amount of AN was added to the aqueous solution of partially acetylated PVA in the presence of potassium peroxydisulfate and heated under stirring. Then the aqueous solution of the graft copolymer—AN graft polymerized to PVA—was obtained, and with this solution a new synthetic fiber made of graft copolymer was prepared by the spinning into saturated aqueous solution of sodium sulfate, heatdrawing, heat-treatment and formalization as in the case of ordinary vinylon. Unfortunately, however, the fibers prepared by this method did not have sufficient tensile strength, although some interest properties were obtained, and moreover the grafted percents of AN could not be raised over ca. 20% for the limited stability of the spinning solution.

In the present work acrylonitrile (AN), methyl methacrylate (MMA), styrene (St) and other vinyl monomers are graft polymerized onto PVA fiber mainly with gamma ray irradiation in order to add some favorable properties of grafted polymers to PVA fiber.

It had been reported by I. Sakurada and T. Okada²⁾ that St, MMA and other monomers could be graft polymerized to PVA films, if PVA films were irradiated with γ -ray during immersion in those monomers at the presence of water. In the

* Some parts of this paper had been reported by the authors in the Journal of the Chemical Society of Japan, Industrial Chemistry Section, 63, 1927 (1960).

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present work these results will be applied to PVA fibers and the properties of grafted PVA fibers will be examined.

It was found that very large amounts of various monomers could be graft polymerized to PVA fibers and some favorable properties could be imparted without lowering tensile strength. For instance, the grafted percents of MMA and St to PVA fiber could be easily reached to 400-600% and that of AN could be reached to 20-30%, though the grafted percents to PVA fiber were generally less than those to PVA film.

THE GRAFT POLYMERIZATION OF SOME MONOMERS TO POLYVINYL ALCOHOL FIBER

The graft polymerizations of St and MMA and AN to PVA fibers were performed by several methods. The results will be briefly described.

The Graft Polymerization of Styrene

About 0.4-0.5 g of the slightly elongated and slightly heattreated PVA fiber, whose degree of polymerization, residual acetyl group contents and degree of swelling for water at 30°C were respectively 1700, 0.1 mol.% and 64%, was immersed in water for 24 hours at 30°C, pressed with a filter paper, sealed in a glass tube containing 20 ml. of styrene (St) in the presence of air, and then irradiated with Co^{60} γ -ray at the rate of 5.6×10^4 r/h. The graft polymerization of St to PVA fiber proceeded during irradiation. Then the treated PVA fiber was taken out from the glass tube and the homopolymer of St was extracted with benzene at 30°C for 48 hours. The grafted percents of St were estimated as the weight increase percents of the fiber by the graft polymerization.

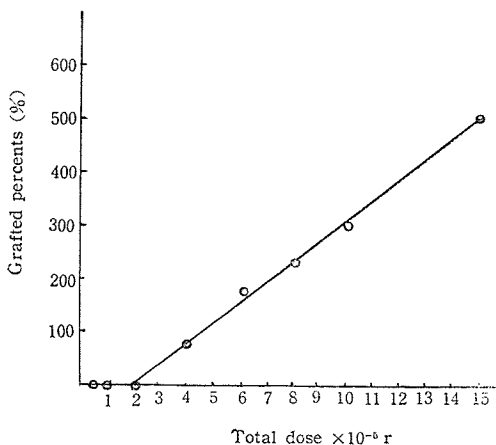


Fig. 1. The graft polymerization of styrene onto PVA fiber by γ -radiation (dose rate 5.6×10^4 r/hr).

One example is shown in Fig. 1. It is shown that the graft polymerization proceeds almost linearly with total dose of irradiation up to about 500% except some induction period.

The Graft Polymerization of Acrylonitrile

PVA fiber was irradiated with Co^{60} γ -ray in acrylonitrile (AN) containing 7 percents of water in the same way as the graft polymerization of St. In this case the homopolymer of AN was extracted with dimethyl formamide at 30°C for 48 hours and the grafted percent was estimated like as in the case of St.

It was recognized that the graft polymerization of AN proceeded, although the maximum grafting percents was only about 20 percent. One experimental example is shown in Fig. 2.

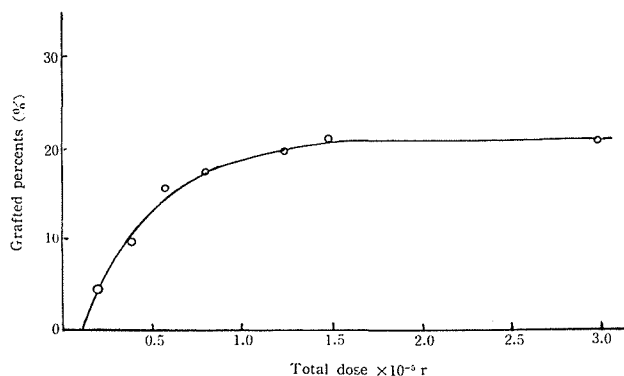


Fig. 2. The graft polymerization of acrylonitrile to PVA fiber by γ -radiation (dose rate 5.6×10^4 r/h.)

The Graft Polymerization of Methyl Methacrylate

PVA fiber was irradiated with Co^{60} γ -ray in the solution which contained methyl methacrylate (MMA), acetone and water (volume ratio = 14 : 56 : 30) in the same way as St and AN. The homopolymer of MMA was extracted with acetone.

The graft polymerization of MMA also proceeds after some induction period. However, this induction period seems to be greatly affected with the slight de-

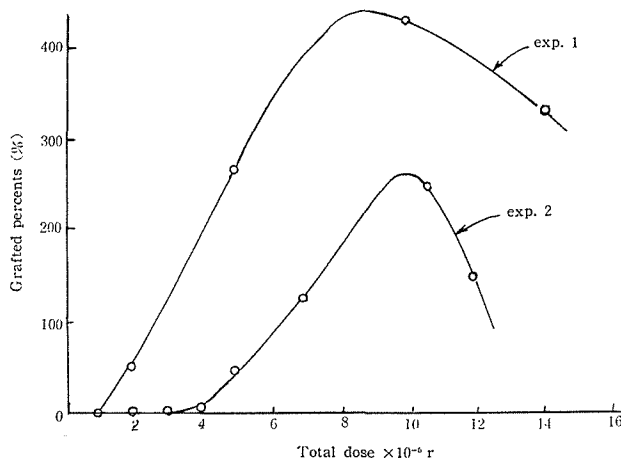


Fig. 3. The graft polymerization of methyl methacrylate to PVA fiber by γ -radiation (dose rate: 5.6×10^4 r/hr).

viation of the grafting condition, so it was difficult to obtain the reproducible result. Moreover, the decrease of grafted percents was almost always recognized at higher total dose. Two experimental results are shown in Fig. 3.

The Graft Polymerization of Styrene and Methyl Methacrylate without Radiation

It had been also reported by I. Sakurada and his coworkers³⁾ that PVA films were highly graft-polymerized with various kinds of monomer, when immersed in monomers in the presence of ferrous or ferric ion. It was found that this method could be also applied for PVA fibers to obtain the highly grafted products without lowering tensile strength.

Experimental results for St and MMA will be described in following.

Methyl methacrylate. Ca. 0.4-0.5 g of PVA fiber was sealed in a glass tube (ca. 30 ml.) with 25 ml. of the solution, containing MMA, acetone, water and ferrous ion (the volume ratio of MMA/acetone/water was 14/56/30 and the concentration of FeSO_4 was 1.5×10^{-4} mol/l and pH of the solution was 3.5) after perfect degassing, and maintained at the temperature of 22°C. The increase of

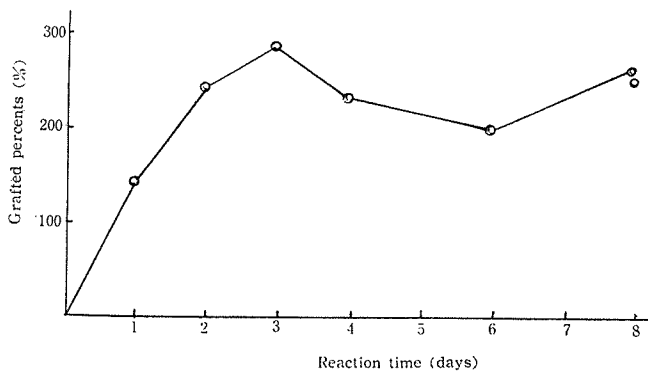


Fig. 4. The graft polymerization of methyl methacrylate onto PVA fiber with ferrous ion catalyzer.

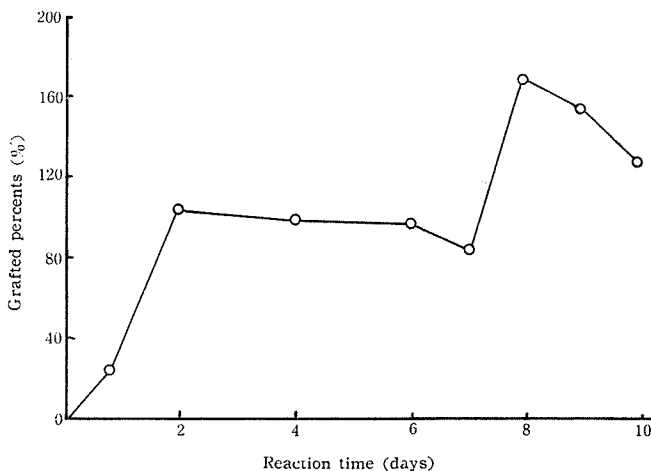


Fig. 5. The graft polymerization of styrene onto PVA fiber with ferrous ion catalyzer.

grafted percents of MMA is shown in Fig. 4.

Styrene. St was grafted almost likely as MMA. The components of the immersing solution were St, methanol, water (volume ratio was 30/70/5) and FeSO_4 (1.0×10^{-4} mol/l). The reaction tube was sealed in the presence of air and maintained at the temperature of 70°C . The grafted percent of St was shown in Fig. 5.

In above described graft polymerizations of St, MMA, and AN, almost untreated PVA fibers were used, but those monomers can be graft polymerized in the similar way onto any different types of PVA fibers such as highly heat-treated or moreover formalized PVA fiber. Though the rate of graft polymerization to such treated PVA fibers seems to be somewhat less than that of an untreated PVA fiber, St and MMA can easily graft polymerize over 100-200 percents onto the treated PVA fibers.

THE PROPERTIES OF GRAFT POLYMERIZED POLYVINYL ALCOHOL FIBERS

The various properties of PVA fibers on which St or MMA was graft polymerized up to various grafted percents were estimated.

The Tensile Properties

The tensile properties of the PVA fibers, on which St was graft polymerized up to various percents, and those of the heat-stretched fibers are shown in Table 1.

Table 1. The Tensile Properties of Polyvinyl Alcohol Fibers, Grafted by Styrene with Co^{60} γ -ray.

Grafted percents %	Graft polymerized fibers				Graft polymerized and heat-stretched (to 3 times, at 150°C) fibers			
	Denier	Tensile strength		Elongation %	Denier	Tensile strength		Elongation %
		g	g/d			g	g/d	
0	1.53	10.3	6.73	25.7	(1.07)*	(10.5)	(9.79)	(11.6)
76.5	5.25	8.84	1.67	119.9	1.77	11.3	6.40	16.5
182	8.75	10.5	1.20	152.3	2.77	11.9	4.29	14.2
229	12.57	10.0	0.80	174.5	4.19	11.9	2.61	9.3
509	19.38	12.6	0.65	19.7	6.48	11.8	1.82	14.9

* Values shown in parentheses are that of 2 times heat-stretched ones, because ungrafted fiber could not be stretched to 3 times.

As can be seen in Table 1, the tensile strengths of fibers per one single fiber are almost constant whatever grafted percents may greatly differ, though the tensile strengths per one denier decrease with the increase of grafted percents because the deniers of the fibers increase with the increase of grafted percents. But it can be seen from the results for the heat-stretched fibers that it is possible to obtain the styrene grafted PVA fiber whose tensile strength exceeds 4-5 g/d, unless the grafted percents exceed 200%.

It is also seen that the elongation increases in accordance with increasing of grafted percents.

Elastic Recovery of Elongation

The elastic recovery of elongation of the St or MMA grafted PVA fibers was

estimated at various elongation and compared with that of the original PVA fiber. It was known by the numerous experiments that the elastic recoveries of the graft polymerized PVA fibers were generally higher than that of those original PVA fibers at the range of relatively lower elongation and less than that at the range of higher elongation.

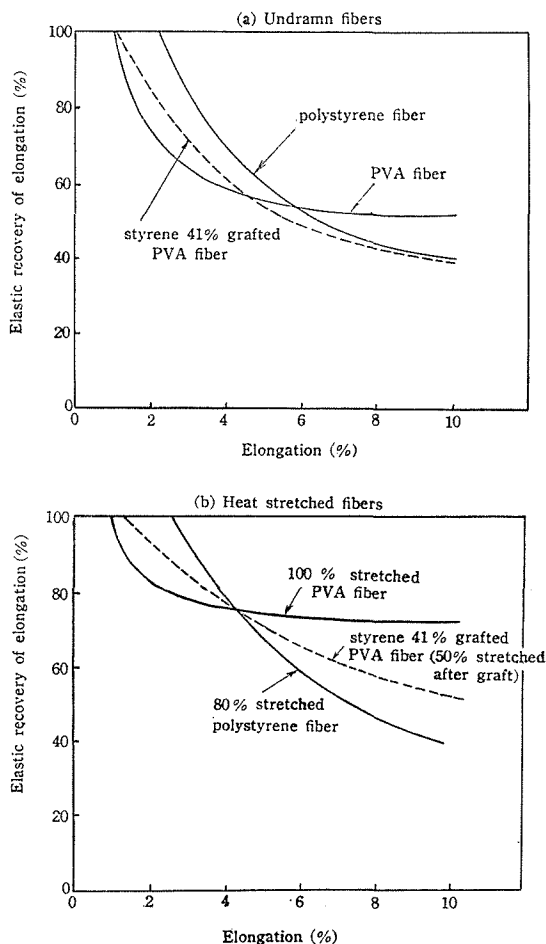


Fig. 6. The elastic recovery of PVA, polystyrene, and styrene grafted PVA fibers.

In Fig. 6 the elastic recovery of St grafted PVA fiber (grafted percents 41%) is plotted against the elongation. Results for the original PVA fiber and a polystyrene fiber are also shown. As can be seen, the elastic recovery of PVA fibers at the range of relatively lower elongation is highly improved and the elastic limit of elongation is highly increased by the graft polymerization of St, especially when stretched at elevated temperature after grafting.

The elastic limit of elongation and elastic recovery at the relatively lower elongation of a polystyrene fiber are generally higher than those of a PVA fiber, while the elastic recovery of the former is lower than that of the latter at the range of higher elongation. The favorable improvement of elastic properties of

Table 2. Tensile properties of St grafted PVA fibers at various temperatures.

Grafted percents of styrene	Tensile strength, g/d					Ultimate elongation, %					Young's modulus, g/d				
	at room temperature	at 50°C	at 100°C	at 150°C	at 170°C	at room temperature	at 50°C	at 100°C	at 150°C	at 170°C	at room temperature	at 50°C	at 100°C	at 150°C	at 170°C
Unstretched fibers															
0	4.15	3.86	3.01	1.96	—**	30	31	41	47	—**	40.6	15.6	11.9	10.8	—
76.5	1.49	1.38	1.27	0.70	—	130	148	143	165	—	15.6	13.6	9.8	1.0	—
182	1.07	1.02	0.66	0.43	—	164	159	160	198	—	15.6	9.4	8.9	0.5	—
495	0.52	0.50	0.38	0.14	—	14	9	29	210	—	12.8	9.5	10.1	4.0	—
3 times stretched fibers*															
0	(6.81)*	—	(4.83)	(4.97)	(5.02)	(12.5)	—	(12.7)	(15.8)	(20.0)	(65.1)	—	(22.7)	(19.9)	(21.3)
76.5	5.13	—	4.54	3.42	2.99	10.3	—	11.8	16.6	14.6	67.4	—	28.8	13.8	12.4
182	2.75	—	2.56	1.76	1.51	10.0	—	10.9	13.3	14.8	40.9	—	24.1	9.3	6.7
495	1.00	—	0.75	0.48	0.32	35.7	—	54.6	72.2	78.0	29.9	—	14.9	6.8	2.2

* These fibers were heat stretched up to 3 times at 150°C except the original PVA fiber which was unable to be stretched up to 3 times. Values for 2 time stretched PVA fiber are shown in brackets for the purpose of reference.

** Undrawn fibers don't stand the temperature of 170°C.

a PVA fiber by the graft polymerization may be attributed to a additional effect of the properties of polystyrene with the graft polymerization.

The Tensile Properties of Graft Polymerized Polyvinyl Alcohol Fiber at Elevated Temperature

The tensile properties of PVA fibers at an elevated temperature are thought to be greatly affected by the graft polymerization of monomers such as St or MMA, because the polymers such as polystyrene or polymethylmethacrylate generally have high thermoplasticity at elevated temperature and relatively lower softening temperature.

The tensile properties of St graft polymerized PVA fibers at various temperatures are shown in Table 2.

As can be expected, it is clear from the data for unstretched fibers that the grafted PVA fibers have higher plasticity than original PVA fibers at an elevated temperature.

St grafted and heat stretched PVA fibers have sufficient tensile properties even at an elevated temperature if the grafted percent is not too high.

It is surprising that these highly grafted PVA fibers have such sufficient tensile properties, when considered that the softening temperature of polystyrene is around 80°C and its melting temperature is 160-170°C. Concerning these phenomena it will be discussed in the final section.

The Change of Length of Graft Polymerized PVA Fibers when Heated in Air

In order to evaluate the heat-resistance and thermoplasticity of the graft polymerized PVA fibers, the changes of length of St or MMA grafted PVA fibers were measured in air at various temperature under various load.

The results for the case in which the load is 0.1 g/d and the rate of heating is 3°C/min. are shown in Fig. 7.

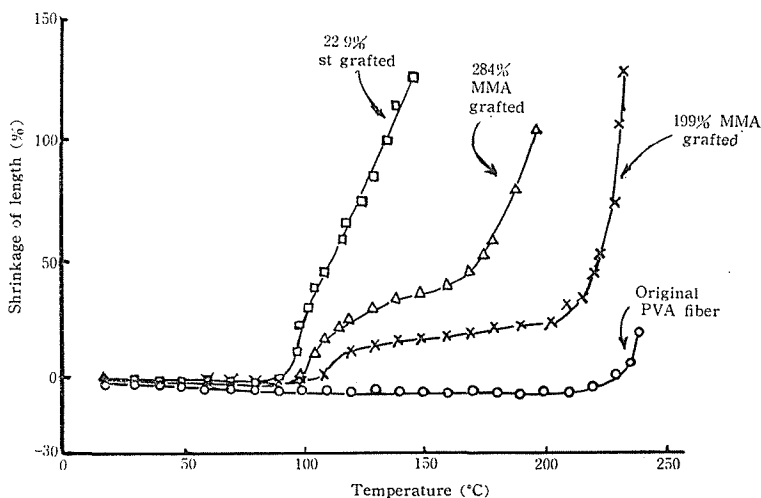


Fig. 7. The change of length of grafted PVA fibers by the heating in air.

It can be seen that the St or MMA grafted PVA fibers show a sudden longitudinal shrinkage at the range of 90-110°C, whereas those original PVA fibers don't show any longitudinal change up to ca. 220°C.

The longitudinal changes of this kind might be affected by the applied load to the fibers during test, but the experimental results for the grafted fibers under various loads indicated almost same softening temperature range, even if some small differences were observed by the change of load and the degree of heat stretching of the fibers. It is clear that these softening temperature ranges are correspond with that of a polystyrene or methyl methacrylate.

The Thermo-Setting Properties of Graft Polymerized PVA Fibers

As described in the above sections, the grafted PVA fibers show the thermo-plasticity at the range of temperature over 90-110°C, then these fibers may be expected to show a superior thermo-setting property in a practical use like ironing. In the matter of fact, it was confirmed by a simple method evaluating the thermo-setting properties as described in following.

Multifilament yarn composed of grafted PVA fibers was wound up around a stainless steel plate in parallel, whose thickness, width and length are respectively 1 mm, 10 mm and 30 mm. Then this plate was inserted between two metal plates which were previously heated at the definite temperature, and heated under the load of 25 g in an air circulated drier. After cooling the yarn was cut along one edge of the steel plate, then a number of small yarn piece of V-shape, each edge 10 mm length, was obtained. The angle of V-shaped test piece was measured immediately and after 20 minutes as a measure of the thermo-setting property. The smaller this angle is, the better thermo-setting property can be expected. The state of the V-shape of yarn was also observed after immersion in cold or

Table 3. The thermo-setting properties of the grafted PVA fibers.
(Thermo-setting was done at 150°C during 2 minutes)

Sample	Angle of V-shaped piece (% to 180°)			State of test piece, in water		
	Grafted percents	immediately after cutting	at 20 min. after cutting	at 15-20°C	at 50°C	at 80°C
Original PVA fiber	0	26.2	34.4	×	×	soluble
Styrene grafted PVA fibers	25.3	22.8	24.8	○	—	×
	45.1	8.0	9.2	⊙	○	○
	93.1	5.4	4.0	⊙	⊙	⊙
	152.5	6.7	6.7	⊙	⊙	○
	260.8	4.8	4.2	⊙	⊙	⊙
MMA grafted PVA fibers	45.9	22.4	23.1	×	×	soluble
	148.0	3.8	3.8	⊙	⊙	⊙
	243.0	4.2	4.2	⊙	⊙	⊙

⊙ Any changes of the form of the heat-setted fibers were entirely not observed.

⊙ The changes of that were practically not observed.

○ Some changes of that were observed.

× V-shape perfectly disappeared.

hot water. The results are summarized in Table 3.

It is clear from Table 3 that the PVA fibers grafted with MMA or St beyond 40-50% have a superior thermo-setting property and the heat-settled form is well remained even if immersed in water at 80°C, though some differences are observed by sorts of grafted monomer or grafted percents.

These thermo-setting properties are useful in the practical use concerning with easiness of ironing of fabric and dimensional stability.

The Resistivity of Graft Polymerized PVA Fibers to Hot Water

An untreated PVA fiber is of course soluble in hot water, but it may be expected to increase the resistivity to hot water by grafting with a hydrophobic polymer. In the matter of fact, the unheat treated PVA fibers graft polymerized with AN or St or MMA are insoluble even in boiling water, though those fibers lose the tensile strength in the water of 90-95°C and in almost all cases show large shrinkage. However, as mentioned in the former section PVA fiber can be graft polymerized, even if it is previously heat-treated or moreover formalized as a water-resist treatment. These graft polymerized fibers of treated PVA fiber show great water resistance and especially the graft polymerized fibers of heat-treated and formalized PVA fibers well resist to boiling water. In addition, even after graft polymerization the PVA fibers can be formalized to resist to boiling water, if the degree of heat-stretching of the original PVA fiber is not so large. For example, the MMA 70% graft polymerized and then formalized one of a slightly stretched and heat-treated PVA fiber had a sufficiently good resistivity to hot water. It shows the shrinkage of only 3% in boiling water.

DISCUSSION

In the former section some properties of the graft polymerized PVA fibers were described and it was shown that those fibers showed some increase of the elasticity and thermoplasticity without much lowering the tensile strength and still remained a considerable tensile strength and other tensile properties even at the temperature at which the grafted polymer such as polystyrene would be softened and lost any tensile properties.

It is reasonable that these changes of the elasticity and thermoplasticity are attributed to the properties of the graft polymerized monomers such as St or MMA which produces a thermoplastic polymer by homopolymerization. However, it is apparently curious that the highly graft polymerized PVA fibers never lose these tensile strengths even at above the temperature at which the grafted polymer would be softened and has lost tensile properties. Moreover, it was observed that these fibers did not adhere mutually, even if these were pressed with the iron of the temperature over the melting temperature of a grafted polymer.

These phenomena may indicate that the components of a grafted polymer are not existent independently with the PVA components in the fibers whatever highly graft polymerized. It might be supposed that either components of the fiber, PVA and grafted polymer, were spreading over in every portion of the grafted

fibers, though the micro structures of these fibers were not so uniform when observed with the photo- or electron-microscope.

Though these conceptions on the structure of the grafted fiber was obtained by our other experiment (which would be reported and discussed in the other paper⁴⁾) concerning with the properties of the differential parts of a graft polymerized PVA film, it might be supposed that the tensile property of the graft polymerized PVA fiber at higher temperature was supported with PVA components, because these still existed as a backbone supporting the dimensional structure whatever highly swelled by the grafted polymer components.

However that may be, the results obtained in this study are not only useful to indicate some way to improve the property of PVA fiber but also much interesting as one example of the change of property of a hydrophilic polymer such as PVA by grafting with a hydrophobic polymer such as polystyrene.

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